マテリアル先端リサーチインフラ利用報告書
ARIM User's Report

【Release：2025.03.11】　【Update：2025.03.11】

課題データ / Project Data

課題番号 Project Issue Number	23JI0001
利用課題名 Title	次世代リチウム空気電池に向けた多元素ハイエントロピー新ナノ合金電極の開発
利用した実施機関 Support Institute	北陸先端科学技術大学院大学 / JAIST
機関外・機関内の利用 External or Internal Use	外部利用/External Use
横断技術領域 Cross-Technology Area	計測・分析/Advanced Characterization
重要技術領域 Important Technology Area	次世代ナノスケールマテリアル/Next-generation nanoscale materials 革新的なエネルギー変換を可能とするマテリアル/Materials enabling innovative energy conversion
キーワード Keywords	Mesoporous High Entropy Nanoalloys, Catalysis, Electrochemical energy storage devices,電子分光/ Electron spectroscopy

利用者と利用形態 / User and Support Type

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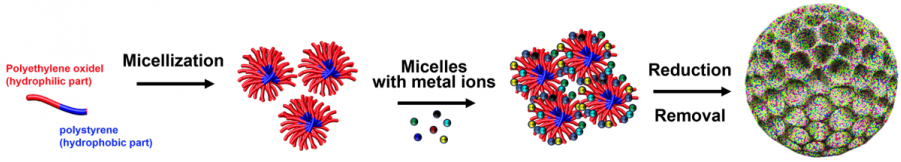
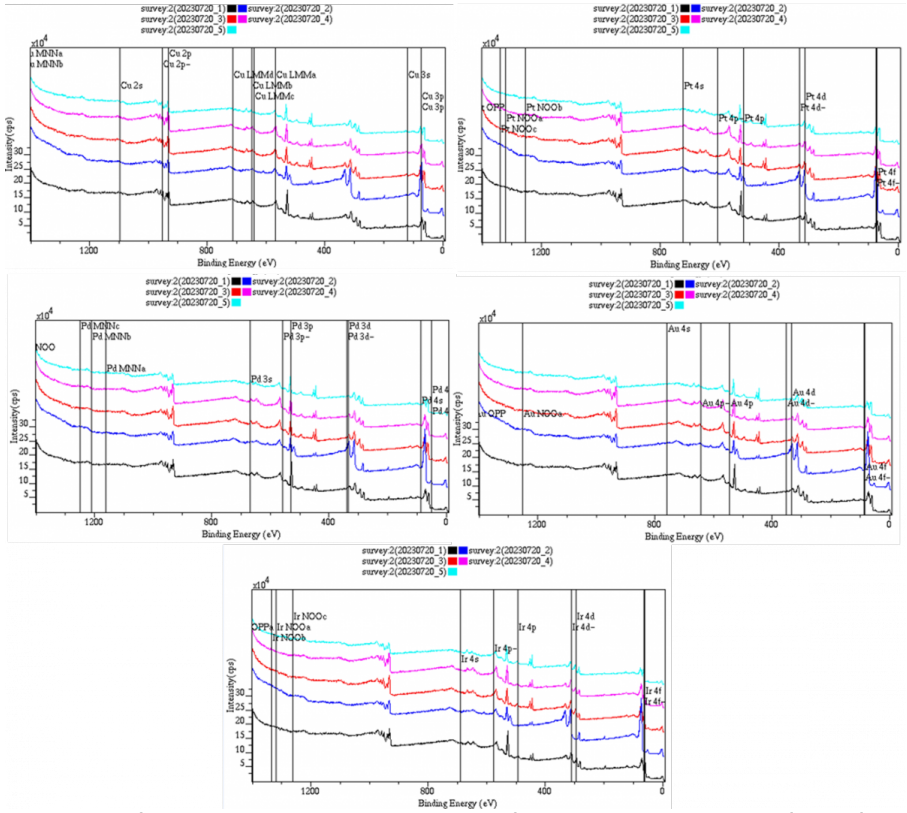
ARIM実施機関支援担当者 Names of Collaborators in The Hub and Spoke Institutes	村上達也
利用形態 Support Type	技術代行/Technology Substitution

利用した主な設備 / Equipment Used in This Project

利用した主な設備 Equipment ID & Name	JI-013：X線光電子分光装置

報告書データ / Report

概要（目的・用途・実施内容） **Abstract (Aim, Use Applications and Contents)**	This work aims to establish a straightforward and versatile synthesis protocol for the production of high entropy nanoalloys (HENAs), with a particular emphasis on low-temperature synthesis that yields mesoporous structures through wet chemical techniques. The mesoporosity enhances the accessibility of surface atoms, thereby improving the overall effective utilization of the material (e.g., mass activity) for targeted applications such as the electrochemical oxidation of low molecular weight alcohols (e.g., methanol) and the oxygen reduction reaction. Furthermore, this structural design promotes better mass and charge transfer during reactions, ultimately extending the longevity of the catalyst.
実験 **Experimental**	The synthesis protocol of mesoporous HENA includes the loading of metal ions (Pt/Pd/Au/Ir and Cu) in copolymer micelles. For this, the di-block copolymer (PS-*b*-PEO) with PS as hydrophobic and PEO as the hydrophilic branch was dissolved in DMF which resulted in a transparent solution. The aqueous metal salt solution upon adding in copolymer-DMF solution results in the micelle formation where the hydrophilic exterior engages the metal ions either through hydrogen bonding and/or electrostatic interaction. Upon introduction of reducing agents like formic acid the metal ions get reduced resulting a multimetallic nanospheres with uniform distribution of individual elements throughout the structure. During the formation of multimetallic nanospheres the micelles act as a soft templating platform which upon careful removal by multiple wash with acetone/ethanol and DI water results the overall porous feature.
結果と考察 **Results and Discussion**	Figure 1 depicts the steps involved in the formation of mesoporous multimetallic (HENA) nanoalloys at relatively low temperatures. The co-polymer-assisted synthesis methodology developed in this study offers a straightforward and effective means of controlling and adjusting the individual elemental content in the HENA spheres. This control is achieved by varying the concentrations of the micelles and precursor metal ions which controls the loading of metal ions loading of copolymer micelles. In this work, we explored various synthesis factors, including reaction temperature, metal loading on di-block copolymers, concentrations of metal ions and copolymers, reaction pH, and different types of reducing agents. The objective was to identify the optimal parameters for designing mesoporous high-entropy nanoalloys (HENAs). We successfully created five different types of mesoporous HENAs composed of Au, Pt, Pd, Ir, and Cu using the synthesis protocols illustrated in Figure 1. One key advantage of HENA-based systems is their surface heterogeneity. The presence of various atom types at the surface results in a diverse array of catalytic active centers resulting in a near continuum of adsorption energies, which is particularly advantageous for facilitating complex electrochemical reactions, such as the oxidation of low molecular weight alcohols, specifically methanol (methanol electro-oxidation, or MOR). This process involves a six-electron transfer and various reaction intermediates and thus requires a potent catalytic system with diverse range of active sites. To investigate the heterogeneous nature of the HENA surface, we employed X-ray photoelectron spectroscopy (XPS), a highly surface-sensitive technique, as shown in Figure 2. The survey spectrum of the AuPtPdIrCu-based mesoporous HENAs clearly exhibits characteristic peaks for Au, Pt, Pd, Ir, and Cu, indicating the heterogeneous surface characteristics that are anticipated to enhance MOR.
図・表・数式 1 **Figures, Tables and Equations 1**	 **Figure 1.** The schematic representation of synthesis protocols for the formation of mesoporous multimetallic (i.e., HENA) nanospheres.

図・表・数式 2 Figures, Tables and Equations 2	 **Figure 2.** The XPS survey spectra of five different sets of AuPtPdIrCu-based high entropy nanoalloys (HENA).
その他・特記事項（参考文献・謝辞等） Remarks(References and Acknowledgements)	The authors acknowledge financial support from the Japan Society for the Promotion of Science (JSPS, No. P22063) and the JST-ERATO Project (JPMJER2003). The authors are also thankful to the Center of Nano Materials and Technology, Japan Advanced Institute of Science and Technology (JAIST) for XPS measurements. The authors acknowledge the English editing facility of Grammarly web, https://app.grammarly.com/ for refining the language and for checking the grammatical errors.

成果発表・成果利用 / Publication and Patents

DOI（論文・プロシーディング） DOI (Publication and Proceedings)	
口頭発表、ポスター発表および、その他の論文 Oral Presentations etc.	
特許出願件数 Number of Patent Applications	0件
特許登録件数 Number of Registered Patents	0件